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(54) STORAGE STABLE CONCENTRATES OF PEROXY-CONTAINING FUNCTIONAL AGENTS

(71) We HENKEL KOMMANDITGESELLSCHAFT AVE AKTIEN a German Company, of 67 Henkelstrasse, 4000 Duesseldorf-Holthausen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to storage stable concentrates for the production and replenishment of peroxy-containing functional agents.

It is known that the solutions of peracetic and perpropionic acid represent functional agents which may be used for various purposes. They are suitable, for example, for the oxidation of organic material generally and for the treatment of hair, straw and textiles. In particular, however, they may be used as microbicidal and virucidal agents. Peracetic acid is preferably used.

However, pure per acids are not only problematical because of their production, but they are also difficult to handle because of their combustibility and the risk of explosion. Thus, in practice, the acids are not used in their pure form, but in mixtures of, for example, 35% to 45% peracetic acid and 40 % to 55 % acetic acid. The proportion of water is generally below 15 %. The disadvantage with these concentrates is that they may only be handled under strict safety regulations because of their pungent smell and their caustic effect upon the user who has to dilute the concentrates initially. If, however, concentrates are produced from, for example, 5 % to 25 % by wt. of per acid alone and the remainder is water, then these are not stable in storage.

It is an object of the present invention to provide concentrates which avoid the above disadvantages. According to the present invention this object is achieved by providing a storage stable concentrate which comprises:-

1. From 0.5% to 20% by weight of an acid selected from peracetic aid, acetic acid, mixtures of peracetic acid and acetic acid, perpropionic acid, propionic acid and mixtures of perpropionic acid and propionic acid,
2. from 25% to 40% by weight of anhydrous H_2O_2 and
3. the remainder to 100% by weight, water.

The concentrates, which are stable in storage and contain H_2O_2, are preferably characterised by a content of 5 % to 10 % by wt. of component (1) and a molar excess of H_2O_2 relative to component (1) (calculated as the monocarboxylic acid) of at least 2 : 1, preferably 3 : 1 to 50 : 1. Preferably component (1) is peracetic acid or a mixture of peracetic and acetic acids.

In the following description the preparation of the concentrates is described by reference to peracetic acid and acetic acid, but it is to be understood that such description applies equally to perpropionic acid and propionic acid.

Production is effected simply by mixing H_2O_2 solution, preferably with a concentration of substantially 33 % by wt., with peracetic acid and, where applicable, acetic acid. The mixtures may also be produced advantageously be merely mixing the concentrated H_2O_2 solution with the appropriate quantity of acetic acid. Since the products are mainly not supplied directly for use but are stored first of all, an appropriate content of peracetic acid is added. If desired, the formation of peracetic acid may be accelerated catalytically by a small quantity of mineral acid (0.1 % to 1 %). However, an addition of this type is generally not required because of the above-mentioned reasons.

Such concentrates, which are produced, for example, from 30 % H_2O_2, 5 % acetic acid and 65 % water, no longer have any disadvantageous smell and are easy to handle, i.e. they can easily be diluted to the concentrations of total-ingredients of 0.1 % to 1 % by weight commonly used in food technology and in the medical sector, without considerable safety measures being necessary.

Because of the many possible uses of the above-described functional agents, for example for the oxidation of organic material generally or for the treatment of hair, straw and textiles, and as microbicidal and virucidal agents, it is advantageous, in many cases, to use these simultaneously with the addition of a wetting agent in order to improve even further the desired properties.

It has been found that stable in storage concentrates of the above-described type are obtained if anionically active wetting agents in the form of alkylbenzene sulphonate, alkyl sulphate and/or alkyl sulphonate are also added in quantities of 0.05 % to 5 % by wt.

Examples of alkylbenzene sulphonates to be considered are those which contain an alkyl residue of 6 to 18 carbon atoms, preferably 9 to 15 carbon atoms. Instead of alkyl-benzene sulphonates, alkyl sulphates or alkyl sulphonates are also considered with an alkyl residue having a chain length of 12 to 18 carbon atoms. If desired, mixtures of the anionically active wetting agents mentioned may also, of course, be used.

It has been shown that the additions mentioned remain stable in the concentrates even over long periods of time and the content of peracetic acid thus also remains constant in the concentrate. If, however, soaps or the conventional non-ionic wetting agents are used for the addition of wetting agents, then adequate stability is not achieved.

The new stable in storage concentrates of the functional agents described may be used for all purposes where an oxidising effect is to be achieved and where the disadvantages of the known pure per acids make it difficult to use them or exclude the possibility of using them. The agents also have the advantage that they are suitable for static disinfecting purposes in order to prevent the propagation of secondary bacteria on machines, such as those used in particular in the food industry, after cleaning. In addition, a long-term effect upon most micro-organisms is produced because of their H_2O_2 portion.

The pH value of the solution for use is still slightly acidic, and the acetic acid residues are extremely small after the disinfecting processes, so that the agents are also suitable for a disinfecting process where rinsing is no longer necessary.

The present invention will now be further illustrated by way of the following examples:-

Example 1

A concentrate for the production of microbicidal agents was produced by mixing

5 % by wt. acetic acid
30 % by wt. anhydrous H_2O_2
65 % by wt. water (including water added as H_2O_2 solution)

The concentrate was left to stand and a sample was taken at specific intervals to determine the content of H_2O_2 and peracetic acid. The results are given in Table 1 below. For comparison purposes, a further concentrate was produced which contained 8 % by wt. of peracetic acid, 8.5% by wt. of acetic acid, 1 % by wt. of H_2O_2 and 82.5 % by wt. of water. Samples were taken from the mixture after specific intervals and the peracetic acid content was determined. The results are given in Table 2. It can clearly be seen that the agents are not stable.

Table 1

Time	H_2O_2 %	Peracetic %
1 week	28.5	3.3
1 month	28.3	3.5
3 months	28.3	3.5
6 months	28.2	3.5

Table 2

Time	% by wt. of per acid
1 h	7.6
10 h	6.1
2 days	3.0
14 days	1.2
1 month	0.6

Example 2

Concentrates of the composition given below (Products A to C) were produced from H_2O_2, acetic acid and water. These concentrates were left to stand for a time and then diluted to form a 0.05 % or 0.2 % by weight of total-ingredients solution respectively. Using the suspension test, the results were determined afterwards according to the guidelines of the Deutsche Gesellschaft fürHygiene und Mikrobiologie (DGHM) (German Society for Hygiene and Microbiology). The values (killing times in minutes) are given in Table 3 below.

The experiments were repeated after the concentrate had been stored over relatively long periods.

	Products (figures in % by wt.)		
	A	B	C
H_2O_2 (anhydrous)	23.1	23.1	23.1
acetic acid	20	10	5
H_2O	56.9	66.9	71.9

Table 3

	Staph. aureus						*E.coli*					
Product	A		B		C		A		B		C	
Concentration	0.05%	0.2 %	0.05%	0.2 %	0.05%	0.2 %	0.05%	0.2 %	0.05%	0.2 %	0.05%	0.2 %
Days	Killing Times in Minutes						Killing Times in Minutes					
10	5	1	5	2.5	10	5	5	1	30	2.5	40	2.5
60	5	1	5	2.5	10	5	5	1	30	2.5	40	2.5
90	5	1	5	2.5	10	5	5	1	30	2.5	40	2.5

Example 3

Using the suspension test according to the guidelines of the DGHM, the killing times for *staphylococcus aureus* were determined by means of mixtures of H_2O_2 and small quantities of acetic acid or propionic acid. The results are given in Table 4 below.

Table 4

ppm H_2O_2	1165	1165	1165
ppm acetic acid		50	
ppm propionic acid			50
Killing time(min.)	20	5	5

Example 4

A concentrate was produced by mixing

5 % by wt. of acetic acid
27.6 % by wt. of anhydrous H_2O_2
1 % by wt. of alkyl-(C_{12}-C_{18}-sulphonate) and
66.4 % by wt. of water (including water added as H_2O_2 solution)

The concentrate was left to stand and a sample was taken at specific intervals to determine the content of anhydrous H_2O_2 and peracetic acid. The results are given in Table 5 below.

Table 5

Stability of the mixtures with the addition of an alkyl sulphonate

20°C Time	% H_2O_2 (anhydrous)	% peracetic acid
initial value	26.2	2.3
1 month	26.1	2.3
3 months	25.1	2.3
6 months	25.0	2.3

Practically the same results are obtained when the concentrates contain 1 % alkyl sulphate (alkyl residue C_{12}-C_{18}) instead of 1 % alkyl sulphonate.

Example 5

In order to check the fungicidal and sporicidal effect, concentrates containing different quantities of wetting agent were produced by mixing

5 % by wt. of acetic acid
27.6 % by wt. of anhydrous H_2O_2
1 or 1.5 % by wt. of dodecylbenzene sulphonate
and
66.4 or 65.9 % by wt. of water (including water added as H_2O_2 solution)

The concentrates were left to stand for a time and diluted to a concentration of total-ingredients of 1% or 2% by weight respectively. The fungicidal and sporicidal effect was determined in the suspension test according to the guidelines of the Deutsche Gesellschaft für Hygiene und Mikrobiologie (DGHM) (German Society for Hygiene and Microbiology) at 20 °C. The results (killing times in minutes) are given in Table 6 below.

Table 6

Fungicidal and sporicidal effect of the concentrate containing different quantities of wetting agent

(Killing times in min.)

Concentrate + % alkylbenzene sulphonate (50%)	Conc. (%) solution for use	1	2	3
without wetting agent	1.0	>60	40	5
	2.0	>60	20	2.5
2.0	1.0	40	5	1
	2.0	20	2.5	1
3.0	1.0	40	5	1
	2.0	20	1	1

1 = *aspergillus*
2 = *pen. camerunense*
3 = *candida albicans*

WHAT WE CLAIM IS:-

1. A storage stable concentrate which comprises:-
   1. from 0.5% to 20% by weight of an acid selected from peracetic acid, acetic acid, mixtures of peracetic acid and acetic acid, perpropionic acid, propionic acid and mixtures of perpropionic acid and propionic acid,
   2. from 25% to 40% by weight of anhydrous H_2O_2 and
   3. the remainder to 100% by weight, water.

2. A storage stable concentrate as claimed in claim 1, which comprises 5% to 10% by wt. of component (1) and a molar excess of H_2O_2 relative to component (1) (calculated as the monocarboxylic acid) of at least 2 : 1.

3. A storage stable concentrate as claimed in claim 2, in which the molar excess of H_2O_2 is in the ratio of 3 : 1 to 50 : 1.

4. A storage stable concentrate as claimed in any one of claims 1 to 3 which also comprises 0.05% to 5% by wt. of anionically active wetting agent in the form of alkylbenzene sulphonate and/or alkyl sulphate and/or alkyl sulphonate.

5. A storage stable concentrate as claimed in claim 4, in which the alkylbenzene sulphonate contains an alkyl residue of 6 to 18 carbon atoms.

6. A storage stable concentrate as claimed in claim 5, in which the alkylbenzene sulphonate contains an alkyl residue of 9 to 15 carbon atoms.

7. A storage stable concentrate as claimed in any one of claims 4 to 6, in which the alkyl sulphate and/or alkyl sulphonate have an alkyl residue to 12 to 18 carbon atoms.

9. A storage stable concentrate as claimed in claim 1 substantially as hereinbefore described and with reference to any one of the examples.

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